

IN THE UNITED STATE PATENT AND TRADEMARK OFFICE

In re application of Akihisa HONGO al. Serial No. 09/762,582 Filed April 12, 2001 SUBSTRATE PLATING METHOD AND APPARATUS

: Docket No. 2001-0133A : Group Art Unit 1753

: Examiner Arun S. Phasge

VERIFYING DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Tomohiro Mori, declare and say:

that I am thoroughly conversant in both the Japanese and English languages; that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of Japanese Patent Application No. H10-239490 filed on August 11, 1998.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that there statements were made with the knowledge that willful false statements and like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this _____4th day of November__, 2005

Tomohiro Mori

TRANSLATOR

(NAME OF DOCUMENT) PATENT APPLICATION

(REFERENCE NUMBER)

EB1689P

(FILING DATE)

August 11, 1998

(DESTINATION)

DIRECTOR GENERAL OF THE PATENT OFFICE

(INTERNATIONAL PATENT CLASSIFICATION)

C23C 18/00

INVENTION) SUBSTRATE PLATING METHOD AND (TITLE OF THE

APPARATUS

(NUMBER OF THE CLAIMS) 5

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(REGISTERED NUMBER FOR PAYMENT) 026996

(THE NAME OF DOCUMENT) DRAWINGS

(AMOUNT)

21000

(LIST OF DOCUMENT FILED)

(THE NAME OF DOCUMENT) SPECIFICATION

(THE NAME OF DOCUMENT) ABSTRACT

(THE NUMBER OF GENERAL POWER OF ATTORNEY) 9112447

(THE NUMBER OF GENERAL POWER OF ATTORNEY) 9501133

NOV 1 0 7005 BUT

(NAME OF DOCUMENT) SPECIFICATION

(TITLE OF THE INVENTION) SUBSTRATE PLATING METHOD AND APPARATUS

(CLAIMS)

(CLAIM 1) A substrate plating method for filling a wiring recess formed in a semiconductor substrate with plating metal, said substrate plating method characterized by:

performing an electroless plating process of forming an initial film on a substrate, and an electrolytic plating process of filling said recess by electrolytic plating while said initial film serves as a feeding layer.

(CLAIM 2) A substrate plating apparatus for filling a wiring recess formed in a semiconductor substrate with plating metal, said substrate plating apparatus characterized by:

an electroless plating tank for forming an initial film on a substrate by electroless plating, an electrolytic plating tank for filling said recess by electrolytic plating while said initial film serves as a feeding layer, and transfer means for transferring the substrate between said tanks.

(CLAIM 3) A substrate plating apparatus for filling a wiring recess formed in a semiconductor substrate with plating metal, said substrate plating apparatus characterized in that:

an electroless plating liquid supply passage for supplying an electroless plating liquid to form an initial

film on a substrate by electroless plating, and an electrolytic plating liquid supply passage for supplying an electrolytic plating liquid to fill said recess by electrolytic plating while said initial film serves as a feeding layer are alternatively switchably provided in the same processing tank.

(CLAIM 4) A substrate plating method characterized in that a pH regulator including no alkali metal is used as a pH regulator for the plating liquid used in the substrate plating method or apparatus according to any one of claims 1 through 3.

(CLAIM 5) A substrate plating method characterized in that the concentration of $CuSO_4 \cdot 5H_2O$ in the electrolytic plating liquid used in the substrate plating method or apparatus according to any one of claims 1 through 3 is in a range of 100 to 150 g/l, and the concentration of H_2SO_4 therein is in a range of 100 to 150 g/l.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(TECHNICAL FIELD TO WHICH THE INVENTION BELONGS)

The present invention relates to a plating method of substrate, and more particularly to a filling method and apparatus for filling a wiring recess or the like formed in a semiconductor substrate with metal to form wiring, such as copper and copper alloy.

(0002)

(PRIOR ART)

Conventionally, in order to form a wiring circuit on a

semiconductor substrate, a film of Al or Al alloy is deposited on a surface of the substrate by sputtering or the like, and then unnecessary portions of the film are removed by chemical dry etching using a patterned mask such as a photoresist. However, as the level of integration of circuits increases, the width of wiring becomes narrower to thus increase current density, resulting in generating thermal stress in the wiring and increasing temperature of the wiring. As a result, the film of Al or Al alloy becomes thinner due to stress migration or electromigration, finally to cause a breaking of the wiring.

(0003)

Hence, much attention has been drawn to copper, which has a lower resistance and higher reliability, as a wiring material. However, it is difficult to form wiring by etching after deposition and patterning, as in conventional Al wiring. Therefore, there has been attempted a damascene process in which a groove for wiring is preformed in a substrate and filled with copper by chemical vapor deposition (CVD), sputtering, plating, or the like, and then unnecessary portions are removed from a surface of the substrate by chemical mechanical polishing (CMP) to form wiring in the groove.

(0004)

Among these processes for filling a wiring groove with copper, much attention has been drawn to a plating process because the plating process has advantages in that the processing cost is lower than that in other processes, that

pure copper material can be obtained, and that a low-temperature process, which is unlikely to damage a substrate, can be performed. The plating methods mainly include electroless plating, which is performed by a chemical process, and electrolytic plating, which is performed by an electrochemical process. The electrolytic plating is generally more efficient than the electroless plating.

(0005)

(PROBLEM TO BE SOLVED BY THE INVENTION)

Since copper is liable to be oxidized, corroded, and diffused into SiO₂, wiring is usually formed after wiring portions on a base material of a substrate are covered with a barrier layer made of metal nitride such as TiN, TaN, and WN. Since the sheet resistance of the barrier layer is prohibitively larger than the resistance of the plating liquid, it has been difficult to perform uniform electrolytic plating on the barrier layer over the surface of the substrate.

(0006)

Conventionally, a seed layer of copper is formed on the barrier layer by sputtering or CVD, and then an electrolytic copper plating process is performed on the seed layer to fill fine recesses formed in the substrate with copper. However, sputtering has difficulty in uniformly depositing a film on walls of the fine recesses, and CVD problematically introduces impurities into the deposited film. Further, when the design rule is further decreased from about 0.18 µm

to 0.10 μm , there is no dimensional margin to form a seed layer having a thickness of 0.02 to 0.05 μm within the recesses.

(0007)

On the other hand, in the electroless plating process, since a plating layer is isotropically grown from side walls or bottom surfaces of the fine recesses, inlets of the recesses are covered with metal grown from the side walls, so that voids are likely to be adversely formed in the recesses. Further, since the plating rate of the electroless plating process is about one-tenth as small as that of the electrolytic plating process, the electroplating process is inefficient.

(0008)

It is, therefore, an object of the present invention to provide a substrate plating method and apparatus which can form wiring with a simple process by efficiently filling a fine recess formed in a semiconductor substrate with plating metal so as to be less likely to cause a void or contamination.

(0009)

(MEANS FOR SOLVING THE PROBLEMS)

According to the present invention defined in claim 1, there is provided a substrate plating method for filling a wiring recess formed in a semiconductor substrate with plating metal, the substrate plating method characterized by performing an electroless plating process of forming an initial film on a substrate, and an electrolytic plating

process of filling the recess by electrolytic plating while the initial film serves as a feeding layer.

(0010)

With this method, an initial film (seed layer) formed by electroless plating, and then the recess in the substrate is filled by electrolytic plating while the initial film serves as the feeding layer. Specifically, an electroless plating process, which has high uniformity, and an electrolytic plating process, which has good qualities in leveling and achieves high-speed filling, are combined with each other. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled series of plating with void-free wiring metal in a Since the greater processes, without sputtering or CVD. part of the recess is filled by electrolytic plating after the formation of the feeding layer, it is possible to maintain a high plating rate and increase the throughput.

(0011)

The electroless plating process and the electrolytic plating process may be performed in the same plating processing tank or may be performed in separate plating Further, an electroless plating process of forming tanks. an initial film on a substrate and an electrolytic plating process of filling the recess by electrolytic plating while the initial film serves as a feeding layer may be performed in the same plating processing tank with the same plating With this method, both of the electroless plating electrolytic plating process can and the process

continuously be performed without changing a processing tank or a plating liquid, so that the above effects can be achieved with a simplified apparatus and process.

(0012)

According to the present invention defined in claim 2, there is provided an substrate plating apparatus for filling a wiring recess formed in a semiconductor substrate with plating metal, the substrate plating apparatus characterized by an electroless plating tank for forming an initial film on a substrate by electroless plating, an electrolytic plating tank for filling the recess by electrolytic plating while the initial film serves as a feeding layer, and transfer means for transferring the substrate between the tanks.

(0013)

With this apparatus, an initial film (seed layer) is formed by electroless plating, and then the recess in the substrate is filled by electrolytic plating while the initial film serves as the feeding layer. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with void-free wiring metal in a series of plating processes, without sputtering or CVD. The electroless plating tank and the electrolytic plating tank should preferably be disposed at locations close to each other which are separated from each other by a partition within the same space of the apparatus.

(0014)

Since the transfer means for the substrate is provided

in addition to the electroless plating tank and the electrolytic plating tank, it is possible to continue from one process to the next process while preventing the state of the surface of the substrate from changing during transferring the substrate. Specifically, the electroless plating tank, the electrolytic plating tank, and any required cleaning tanks should preferably be disposed close to each other so that the substrate can be transferred without exposing the surface of the substrate to the atmosphere after the plating process or the rinsing process. Such a function may also be provided in the transfer means itself.

(0015)

According to the present invention defined in claim 3, there is provided an substrate plating apparatus for filling a wiring recess formed in a semiconductor substrate with plating metal, the substrate plating apparatus characterized in that an electroless plating liquid supply passage for supplying an electroless plating liquid to form an initial substrate by electroless plating, a electrolytic plating liquid supply passage for supplying an recess by electrolytic plating liquid to the fill electrolytic plating while the initial film serves as a feeding layer are alternatively switchably provided in the same processing tank.

(0016)

With this apparatus, an initial film (seed layer) is formed by electroless plating, and then the recess in the

filled by electrolytic plating while the is initial film serves as the feeding layer. Accordingly, the recess having a barrier layer of a high resistance can efficiently be filled with void-free wiring metal in a series of plating processes, without sputtering or CVD. Since the electroless plating process of forming the initial film on the substrate and the electrolytic plating process of filling the recess can sequentially be the same processing tank, the time performed in transfer the substrate equipment required to eliminated, and the state of the surface of the substrate can be prevented from changing in quality or the like. A cleaning liquid supply passage for supplying a cleaning liquid to clean a substrate may be provided to perform a cleaning process in the same processing tank.

(0017)

The processing tank may comprise a hermetically sealed tank with a parallel flow. With this arrangement, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus efficiently perform an plating process with sufficient flowability of the plating liquid.

(0018)

According to the present invention defined in claim 4, there is provided a substrate plating method characterized in that a pH regulator including no alkali metal is used as a pH regulator for the plating liquid used in the substrate plating method or apparatus according to any one of claims 1

through 3. With this method, the plating process can be performed while preventing harmful metal from contaminating the substrate.

(0019)

According to the present invention defined in claim 5, there is provided a substrate plating method characterized in that the concentration of $CuSO_4 \cdot 5H_2O$ in the electrolytic plating liquid used in the substrate plating method or apparatus according to any one of claims 1 through 3 is in a range of 100 to 150 g/l, and the concentration of H_2SO_4 therein is in a range of 100 to 150 g/l. With the electrolytic plating having good qualities in leveling, void-free filling can be achieved.

(0020)

(EMBODIMENTS OF THE INVENTION)

Embodiments according to the present invention will be described below with reference to the accompanying drawings. As shown in FIG. 1, a plating apparatus is disposed on a rectangular installation floor 10. Load/unload units 14a, 14b and two rinsing and drying devices 60 for post-processing a substrate after the plating process are disposed in a clean zone 13 positioned at one side of the installation floor 10, and a transfer device (first transfer robot) 61 for transferring a substrate is provided between these components. A second transfer robot 62 movable on a rail is disposed at a central portion of a contaminated zone 12 positioned at the other side of the installation floor 10. An SnCl₂ solution tank 16 containing SnCl₂ solution used

as an activator for plating, a rinsing tank 17, a PdCl₂ solution tank 18 containing PdCl₂ solution used as a catalyst for electroless plating, and a rinsing tank 19 are disposed in order on one side of the second transfer robot 62. An electroless plating tank 20, a rinsing tank 21, an electrolytic plating tank 22, and a rinsing tank 23 are disposed in order on the other side of the second transfer robot 62. The rinsing tanks 17, 19, 21 and 23 may be provided as needed.

(0021)

Each of these processing tanks 16-23 has basically the same shape and structure, and, as shown in FIG. 2, comprises a processing container body 50 having a rectangular plate shape with a recess 50a forming a processing chamber 52 therein, and a cover 51 capable of opening and closing a front opening portion of the processing container body 50. A packing 53 is mounted at a peripheral portion of the processing container body 50 to maintain the water-tightness of the processing container body 50 when the cover 51 is closed so as to be brought into close contact with the processing container body 50. On the other hand, a holding member for detachably holding a substrate W is provided on an inner side of the cover 51, and a sensor (not shown) is provided for detecting the existence of a substrate W on the holding member.

(0022)

In the processing tank (electrolytic plating tank) 22 for performing electrolytic plating, a plate-like anode

electrode (anode) 54 is mounted on the bottom of the recess 50a in the processing container body 50 in parallel with the processing chamber 52, and a shielding plate 55 made of a dielectric material, which has an opening 55a formed therein for regulating the electric field on a plating surface of the substrate W, is disposed at the opening end of the recess 50a. The other processing tanks are not provided with the anode electrode 54 or the shielding plate 55.

(0023)

An upper header 56 and a lower header 57 are mounted on the top and bottom of the processing container body 50 and communicated with the processing chamber 52 via a plurality of through-holes 56a, 57a, respectively. Thus, for example, a processing liquid is supplied from the lower header 57 to the upper header 56 to form a parallel flow along the surface of the substrate to be plated, as shown in FIG. 3. As shown in FIG. 4, processing liquid circulating devices 33 each having a reservoir tank 31 and a circulating pump 32 are provided below the processing tanks 16-23, and a supply pipe 34 and a return pipe 35 extending from the processing liquid circulating device 33 are connected to the lower header 57 and the upper header 56.

(0024)

Since, as described above, the plating tanks 20, 22 are hermetically sealed processing tanks with a parallel flow, a plating liquid can flow along the surface of the substrate at a high speed even in a small space to thus efficiently perform an plating process with sufficient flowability of

the plating liquid. Further, since the processing tanks 16-23 are vertically disposed, bubbles in fine recesses formed in the substrate W can easily flow out therefrom during the plating process or the like. Therefore, uniformity of the plating reaction and the processing rate can be increased, and simultaneously the installation area of the processing tanks 16-23 can be reduced to achieve an efficient arrangement of the processing tanks.

(0025)

In this embodiment, the transfer robot 62 comprises a hexaxial robot having a plurality of arms 63 with a hand 64, which is provided on an end of the arms 63 and is capable of opening and closing (see FIG. 5). A plurality of rollers 65 are rotatably supported on an inner surface of the hand 64. A temporary holding stage 67 having a plurality of supports is provided in the clean zone 13 and used for temporarily holding a substrate W to be transferred between the clean zone 13 and the contaminated zone 12.

(0026)

Next, the plating process according to the plating apparatus thus constructed will be described below with reference to FIGS. 6 and 7. A substrate W held on the load/unload unit 14a, 14b is taken out by the first transfer robot 61, which places the substrate W on the temporary holding stage 67. The second transfer robot 62 introduces the substrate W into the contaminated zone 12, and, if necessary, the substrate W is inserted into the processing container body 50 of the activation tank 16, which performs

an activation process with a processing liquid containing an activator such as $SnCl_2$. Next, the substrate W is transferred to the adjacent rinsing tank 17 and rinsed therein. Further, the substrate W is subjected to an catalyst application process in the catalyst application

(0027)

tank 18.

In this process, Sn2+ ions from the activator are adsorbed by the surface of the substrate W in the activation tank 16, and these ions are oxidized into Sn^{4+} in the catalyst application tank 18. On the other hand, Pd2+ ions are reduced into Pd metal, and the Pd metal is deposited on the surface of the substrate W to serve as a catalyst for following electroless plating process. A single catalyst containing Pd/Sn colloids may be used in this In this embodiment, the catalyst application process. process described above is performed in the activation tank 16 and the catalyst application tank 18 forming a portion of the plating apparatus. However, the catalyst application process may be performed in a separate apparatus, and then the substrate W may be transferred to the plating apparatus. It is possible to dispense with the activation process and/or the catalyst application process in some cases, depending on a material or a state of the inner surface of the recess formed in the semiconductor substrate.

(0028)

The second transfer robot 62 further transfers the substrate W to the electroless plating tank 20, where the

electroless plating process is performed with a predetermined reducing agent and a predetermined plating liquid. With this process, as shown in FIGS. 7(a) and 7(b), an electroless plating layer 41 is formed on the inner surface of a barrier layer 40. In this case, electrons generated at the solid-liquid interface due to decomposition of the reducing agent are applied to Cu²⁺ via the catalyst on the surface of the substrate, and hence Cu metal is deposited on the catalyst to form a copper film layer 41. In addition to Pd, other transition metals such as Fe, Co, Ni, Cu, and Ag may be used as the catalyst.

(0029)

Next, the substrate W is transferred to the electrolytic plating tank 22 by the transfer robot, and the copper film layer 41 formed by the electroless plating process is connected to an electrode to perform an electrolytic plating process with a predetermined plating liquid. Thus, the recess 42 is filled with electrolytic plating metal 43, as shown in FIGS. 7(c) and 7(d).

(0030)

After the electrolytic plating process is completed, the substrate is taken out by the second transfer robot, transferred to the rinsing tank, rinsed therein, and then placed on a second temporary holding stage 85. The first transfer robot 61 holds the substrate, transfers it to the rinsing and drying device 60 to perform final cleaning and drying, and returns it to the load/unload unit 14a, 14b. The substrate is finally transferred to CMP (chemical

mechanical polishing apparatus) to remove unnecessary plating metal from the surface of the substrate by a chemical mechanical polishing process.

(0031)

FIG. 8 shows a plating apparatus according to another embodiment of the present invention. Processing liquid circulating devices 33a, 33b, 33c for circulating and supplying different processing liquids (electroless copper plating liquid, cleaning water, and electrolytic copper plating liquid) to the vertical processing tank 24, which has the same structure as in the previous embodiment, are provided switchably by switching valves 36a-36c and 37a-37c. The processing tank 24 comprises a processing container body 50 having an anode electrode (anode) 54 and a shielding plate 55 therein so as to perform an electrolytic plating process.

(0032)

In this embodiment, for example, after the electroless plating process is completed, the liquid is returned to the reservoir tank 31a. A rinsing water circulating pump 32b is operated to introduce rinsing water into the processing tank 24, and then an electrolytic plating liquid is introduced from the reservoir tank 31c into the processing tank 24. After the electrolytic plating process is completed, a rinsing process is similarly performed. Thus, it is possible to eliminate problems such that plating liquids are mixed with each other. In this embodiment, the electroless copper plating process, the cleaning process, the

electrolytic copper plating process, the cleaning process, and other processes can continuously be performed in the same processing tank 24 simply by changing processing liquids without moving the substrate W. Therefore, the present embodiment can decrease the number of the required tanks as compared to the previous embodiment and can eliminate the need of a transfer robot for transferring a substrate between tanks, thereby reducing the installation floor. Further, the throughput can be increased because the transferring time can be eliminated.

(0033)

FIG. 9 shows a processing tank 25 which continuously performs an electroless plating process and an electrolytic plating process with the same processing liquid. processing tank 25 can perform an electrolytic plating process as with the processing tank shown in FIG. 8. this apparatus, after an electroless plating process is performed, an electrolytic plating process is directly performed by application of a small current of 0.2 A/dm2 or In this case, an electroless plating liquid is used. as a plating liquid, and TMAH is used instead of NaOH or KOH, which is usually used as a pH regulator for electroless plating, in order to prevent the semiconductor substrate from being contaminated. TMAH is an organic alkali chemical including a methyl group. It is necessary to avoid using a reducing agent liable to be decomposed, such as formalin, which has commonly been used.

(0034)

Conventionally, in through-hole plating of a printed circuit board, throwing power has been improved by a high throwing power bath having a low Cu concentration (CuSO₄·5H₂O; 10-80 g/l). However, when trenches and via holes of a semiconductor substrate are plated, not only throwing power but also leveling of plating are required in order to prevent generation of voids. Further, since the high throwing power bath is easily influenced by the flow of a plating liquid, it is desirable to use a plating liquid having an intermediate to high increased concentration so as to be less likely to be influenced by the flow.

(0035)

thinas were examined under the above preconditions. As a result, conventionally used baths such low concentration bath having a CuSO₄ · 5H₂O concentration of 15-80 g/l (high throwing power bath), which is superior in throwing power, or a high concentration bath having a CuSO₄ 5H₂O concentration of 150-220 g/l (decorative bath), which is superior in leveling of plating, were found not to be appropriate. An intermediate concentration bath having a CuSO₄·5H₂O concentration of 100-150 g/l was found to be appropriate for a damascene plating process of a substrate which combines semiconductor an electroless plating process and an electrolytic plating process.

(0036)

(EFFECTS OF THE INVENTION)

As described above, according to the present invention, an initial film (seed layer) is formed by electroless

plating, and then a recess in a substrate is filled by electrolytic plating while the initial film serves as a feeding layer. Accordingly, the recess having a barrier layer of a high electrical resistance can efficiently be filled with void-free wiring metal in a series of plating processes, without sputtering or CVD. Therefore, the present invention can provide a substrate plating method and apparatus which can form wiring with a simple process by efficiently filling a fine recess formed in a semiconductor substrate with plating metal so as to be less likely to cause a void or contamination.

(BRIEF DESCRIPTION OF THE DRAWINGS)

(FIG. 1)

FIG. 1 is a plan view of a plating apparatus according to a first embodiment of the present invention.

(FIG. 2)

FIG. 2 is a side view showing a processing tank of the plating apparatus shown in FIG. 1.

(FIG. 3)

FIG. 3 is a cross-sectional view of the processing tank taken along line A-A in FIG. 2.

(FIG. 4)

FIG. 4 is a schematic view showing processing tanks used in the plating apparatus shown in FIG. 1 and circulating passages of processing liquids.

(FIG. 5)

FIG. 5 is a side view of the plating apparatus shown in FIG. 1.

(FIG. 6)

FIG. 6 is a flowchart showing processes performed in the plating apparatus shown in FIG. 1.

(FIG. 7)

FIGS. 7(a) through 7(d) are schematic diagrams showing a process of plating a recess formed in a substrate.

(FIG. 8)

FIG. 8 is a schematic view showing a processing tank used in a plating apparatus and circulating passages of processing liquids according to a second embodiment of the present invention.

(FIG. 9)

FIG. 9 is a schematic view showing a processing tank used in a plating apparatus and circulating passages of a processing liquids according to the third embodiment of the present invention.

(DESCRIPTION OF THE REFERENCE NUMERALS AND SIGNS)

- 10 installation floor
- 12 contaminated zone
- 13 clean zone
- 16, 18 preprocessing tank
- 17, 19, 21, 23 cleaning tank
- 20 electroless plating tank
- 22 electrolytic plating tank
- 24, 25 common processing tank
- 50 processing container body
- 50a recess
- 51 cover

- 52 processing chamber
- 53 packing
- 54 anode electrode
- 55 shielding plate
- 55a opening
- 56 upper header
- 57 lower header
- 56a, 57a through-holes
- 60 rinsing and drying device
- 61, 62 transfer robot

(NAME OF DOCUMENT) ABSTRACT

(ABSTRACT)

(PROBLEM) The present invention provides a substrate plating method and apparatus which can form wiring with a simple process by efficiently filling a fine recess formed in a semiconductor substrate with plating metal so as to be less likely to cause a void or contamination.

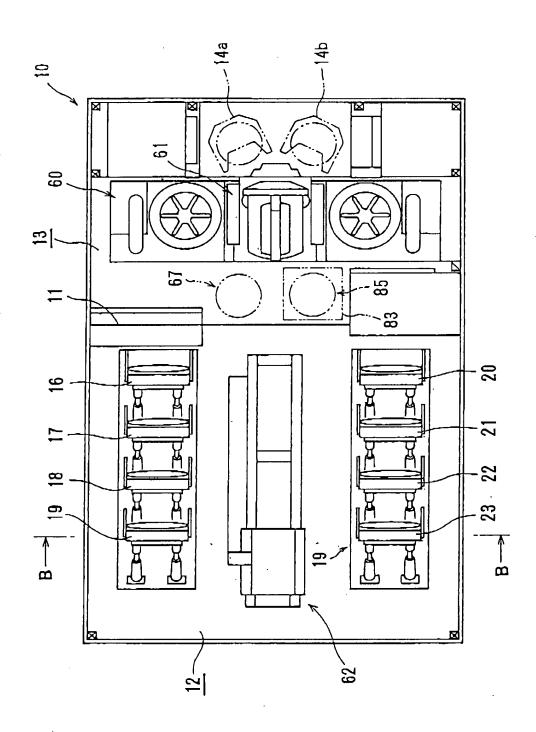
(MEANS FOR RESOLUTION) In a substrate plating apparatus for filling a wiring recess 42 formed in a semiconductor substrate W with plating metal 43, an electroless plating tank 20 for forming an initial film 41 on a substrate by electroless plating, a cleaning tank 21, and an electrolytic plating tank 22 for filling the recess by electrolytic plating while the initial film serves as an electrode are provided close to each other, and transfer means 62 is provided for transferring the substrate between the tanks.

(SELECTED FIGURE) FIG. 1

-1-

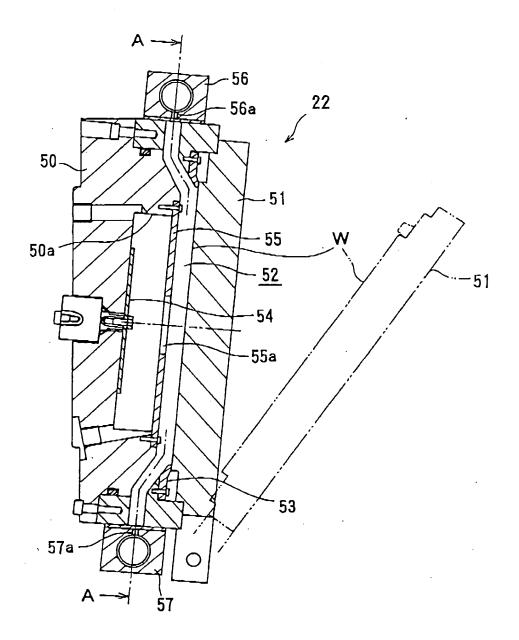


[FIG. 1]



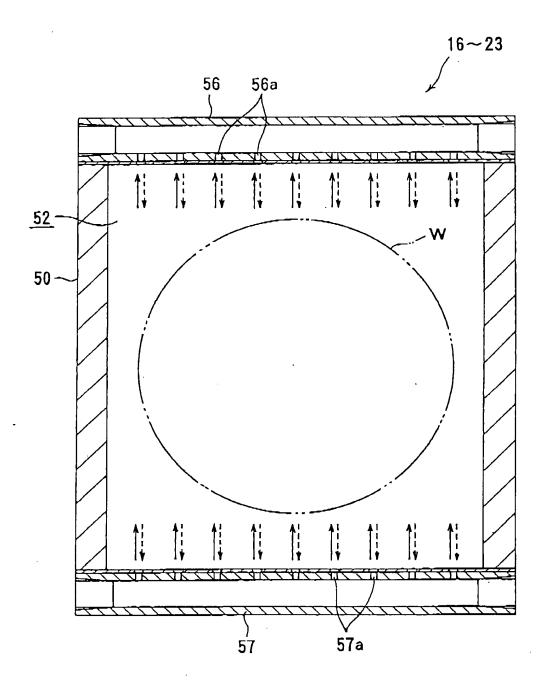
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[FIG. 2]



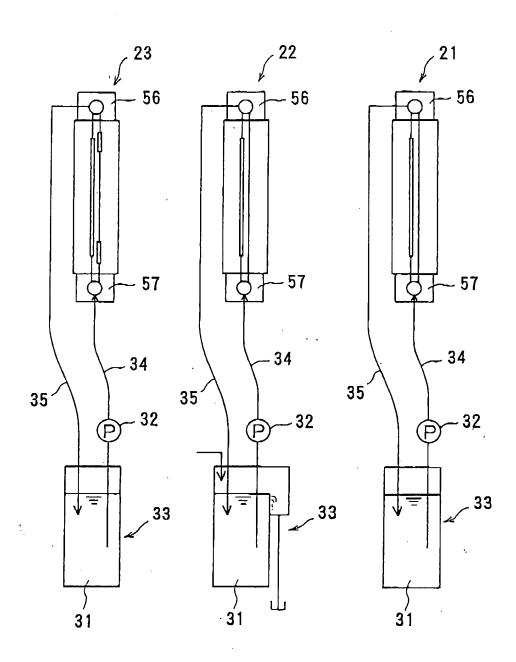
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[FIG.3]



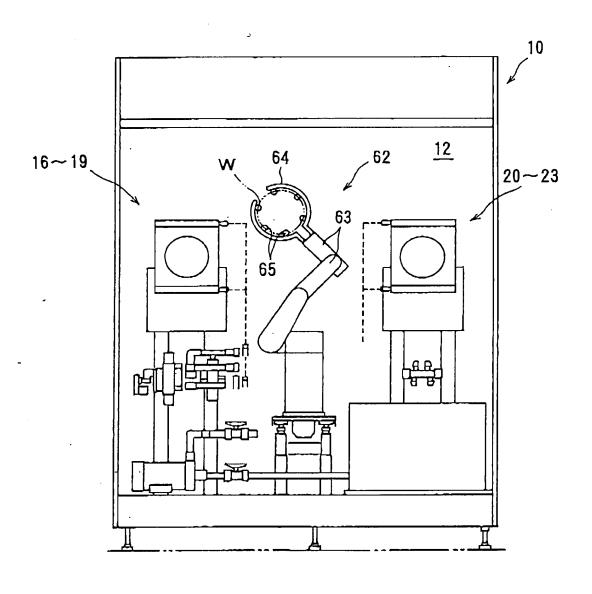
- 4 -

[FIG. 4]



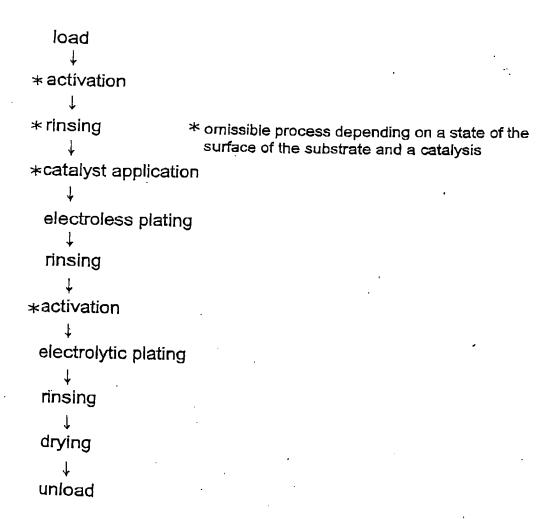
- 5 -

[FIG. 5]



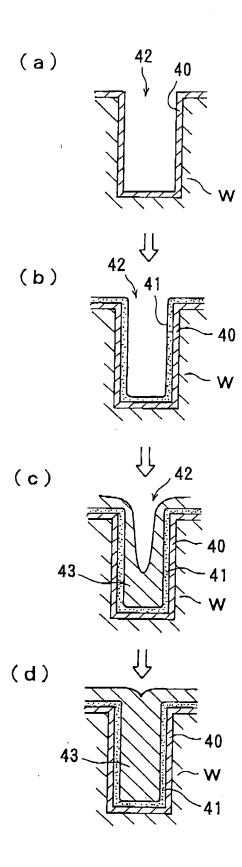
- 6 -

[FIG. 6]



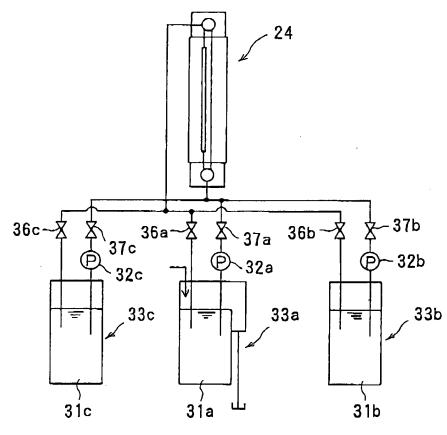
- 7 –

[FIG. 7]



-8-

[FIG. 8]



[FIG. 9]

